

SPECIFICATION

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DRYING PROCESS FOR LOW-K DIELECTRIC FILMS

Background

- [0001] This disclosure relates generally to a method for drying and removing contaminants from low-k dielectric films.
- [0002] Recently, much attention has been focused on developing low k dielectric thin films for use in the next generation of microelectronics. As integrated devices become smaller, the RC-delay time of signal propagation along interconnects becomes one of the dominant factors limiting overall chip speed. With the advent of copper technology, R has been pushed to a practical lowest limit so attention must be focused on reducing C. One way of accomplishing this task is to reduce the average dielectric constant k of the thin insulating films surrounding interconnects. The dielectric constant of traditional silicon dioxide insulative materials is about 3.9. Lowering the dielectric constant below 3.9 will provide a reduced capacitance.
- [0003] The low k dielectric materials used in advanced integrated circuits typically comprise organic polymers or oxides and have dielectric constants less than about 3.5. The low k dielectric materials can be spun onto the substrate as a solution or deposited by a chemical vapor deposition process. Important low k film properties include thickness and uniformity, dielectric constant, refractive index, adhesion, chemical resistance, thermal stability, pore size and distribution, coefficient of thermal expansion, glass transition temperature, film stress, and copper diffusion coefficient.
- [0004] In fabricating integrated circuits on wafers, the wafers are generally subjected to many process steps before finished integrated circuits can be produced. Low-k dielectric materials can be sensitive to some of these process steps. For example,

plasma used during an "ashing" step can strip both photoresist material as well as remove a portion of the low-k dielectric film. Ashing refers to a plasma stripping process by which residual photoresist and post etch residues are stripped or removed from a substrate upon exposure to the plasma. The ashing process generally occurs after an etching or implant process has been performed in which a photoresist material is used as a mask for etching a pattern into the underlying substrate or for selectively implanting ions into the exposed areas of the substrate. The remaining photoresist and any post etch or post implant residues on the wafer after the etch process or implant process is complete must be removed prior to further processing for numerous reasons generally known to those skilled in the art. The ashing step is typically followed by a wet chemical treatment to remove traces of the residue, which can cause further degradation of the low k dielectric and may cause increase in the dielectric constant.

[0005] Alternatively, the photoresist can be removed by the use of wet strippers. Wet strippers include acids, bases, and solvents as are known to those skilled in the art. The particular wet strippers used are well within the skill of those in the art. For example, nitric acid, sulfuric acid, ammonia are commonly employed as wet strippers. In operation, the substrate is immersed, puddled, streamed, sprayed or the like by the wet stripper and subsequently rinsed with deionized water.

[0006] After ashing or wet stripping of the photoresist, a rinsing step is typically employed to remove the stripper, contaminants and/or photoresist residuals. Typically, the rinsing step employs deionized water.

[0007] It is important to note that ashing processes significantly differ from etching processes. Although both processes may be plasma mediated, an etching process is markedly different in that the plasma chemistry is chosen to permanently transfer an image into the substrate by removing portions of the substrate surface through openings in a photoresist mask. The plasma generally includes high energy ion bombardment at low temperatures to remove portions of the substrate. Moreover, the portions of the substrate exposed to the ions are generally removed at a rate equal to or greater than the removal rate of the photoresist mask. In contrast, ashing processes generally refer to selectively removing the photoresist mask and any

polymers or residues formed during etching. The ashing plasma chemistry is much less aggressive than etching chemistries and is generally chosen to remove the photoresist mask layer at a rate much greater than the removal rate of the underlying substrate. Moreover, most ashing processes heat the substrate to temperatures greater than 200 °C to increase the plasma reactivity. Thus, etching and ashing processes are directed to removal of significantly different materials and as such, require completely different plasma chemistries and processes. Successful ashing processes are not used to permanently transfer an image into the substrate. Rather, successful ashing processes are defined by the photoresist, polymer and residue removal rates without affecting or removing underlying layers, e.g., low k dielectric layers.

[0008] Solvents, such as those comprising the wet chemical treatment or wet strippers, can adhere, become adsorbed and/or trapped in pores of the low k dielectric film. This entrainment can cause an increase in the dielectric constant of the film, thus defeating the purpose of using the low-k dielectric. An increase in dielectric constant undesirably affects interconnect capacitance and cross talk. Moreover, trapped cleaning chemicals can also lead to metal corrosion and reduced device reliability since a surface of the dielectric layer typically abuts a conductive metal layer. These problems are exacerbated for those low k dielectrics that contain pores.

[0009] These prior art chemical formulations include strong reagents such as strong inorganic acids, strong bases and/or reactive amine containing compounds. However, such strong reagents can cause unwanted further removal of metal or insulator layers remaining on the wafer and are therefore undesirable in many instances. Additionally, strippers containing both amine component(s) and water may corrode metal, particularly copper, aluminum and aluminum-copper alloys.

[0010] Various methods have been disclosed in the art for removing or reducing the amounts of solvent trapped within the low k dielectric film. For example, You et al., in U.S. Patent No. 6,235,453, describe a plasma treatment at the end of the ashing process, (employs a different plasma chemistry than the ashing process) that seals the surface of the low k dielectric film layer to prevent solvent adsorption in a subsequent wet chemical treatment. However, it has been found that the so-called protective layer

provided by the plasma treatment does not eliminate solvent adsorption and as such does not eliminate the need for a drying step. Moreover, the use of the plasma treatment increases the dielectric constant of the dielectric film layer method by virtue of the treatment. You et al. also describe a method for removing or reducing trapped solvents by employing heat and/or a vacuum. However, the described drying process is relatively slow and relies on the volatility of the contaminants being sufficiently volatile to be outgassed from the low k dielectric film layer. As previously described, some of the contaminants are residual photoresist materials, which are based on polymers and typically are not sufficiently volatile to be removed by the heat and/or vacuum processing by itself.

Brief Summary

- [0011] Disclosed herein is a drying process for removing moisture and contaminants from a substrate having a low k dielectric layer thereon in a process chamber. The process comprises exposing the low k dielectric layer to photons; and simultaneously with, prior to, or subsequent to the photon exposure, exposing the substrate to a process effective to remove the contaminants without causing degradation of the low k dielectric layer, wherein the process is selected from the group consisting of a heat process, a vacuum process, an oxygen free plasma process, and combinations thereof.
- [0012] In another embodiment, a process for removing contaminants adsorbed, adhered, or trapped within a low k dielectric layer, wherein the contaminants comprise residual water, moisture, silanols, residual plasma or wet etch chemistries residuals of wet clean chemistries, acids, bases, and solvents is described. The process comprises exposing the low k dielectric layer in a process chamber to radiation comprising a wavelength of about 150 nanometers to about 500 nanometers; and exposing the substrate to oxygen free plasma, or heat, or a vacuum, or a combination thereof to remove the contaminants without causing degradation of the low k dielectric layer.
- [0013] The above described and other features are exemplified by the following figures and detailed description.

Brief Description of the Drawings

[0014] Referring now to the figures, which are exemplary embodiments and wherein the like elements are numbered alike:

[0015] Figure 1 illustrates a cross section of an exemplary exposure tool for drying a low k dielectric layer; and

[0016] Figure 2 is a FTIR spectra of before and after drying results for a porous doped oxide low-k dielectric film.

Detailed Description

[0017] A process for drying and removing contaminants from low-k dielectric films is described herein. The drying process generally comprises exposing a surface of the low k dielectric film to photons, and simultaneously, prior to, or subsequently applying plasma, or heat or a vacuum, or a combination of two or more of the foregoing processes to remove the contaminants adhered to, adsorbed, and/or trapped by the low k dielectric layer. The photons could be included in ultraviolet (UV), x-ray, and/or other forms of electromagnetic radiation. In a preferred embodiment, the source of photons is from a UV light exposure.

[0018] Preferably, the drying process follows an ashing and/or wet stripping process to remove residues and solvents adhered to, adsorbed, or trapped by the low k dielectric layer. While not wanting to be bound by theory, it is believed that upon photon exposure of the low k dielectric layer, excitation, scission and/or fragmentation of molecular bonds of the contaminants contained therein or thereon occurs, which facilitates the removal of these contaminants. The species generated by excitation, scission and/or fragmentation exhibit greater volatility and can be removed with the plasma or heat or vacuum treatment or the combination of two or more of the foregoing processes applied to the substrate simultaneous with or subsequent to the photon exposure.

[0019] Low k dielectrics are hereinafter defined as those insulating materials suitable for use in the manufacture of integrated circuits or the like having a dielectric constant less than about 3.5. Low k dielectrics can generally be categorized as one of two types: organic, and doped oxides. Examples of organic low k dielectric materials include polyimides, benzocyclobutene, parylenes, diamond-like carbon, poly(arylene

ethers), cyclotenes, fluorocarbons and the like, such as those dielectrics commercially available under the trademarks SiLK, or BCB. Examples of doped oxide low k dielectric materials include methyl silsesquioxane, hydrogen silsesquioxanes, nanoporous oxides, carbon doped silicon dioxides, and the like, such as, for example, those dielectrics commercially available under the trademarks CORAL, BLACK DIAMOND and AURORA. Both types of low-k materials exist in dense and porous versions. Porous versions thereof are commercially known under trademarks such as LKD, ORION, BOSS, or porous SiLK. Other low k dielectric materials will be apparent to one of ordinary skill in the art in view of this disclosure.

[0020] As previously disclosed, the photons could be included in ultraviolet (UV), x-ray, and/or other forms of electromagnetic radiation. For exemplary purposes, reference will now be made in detail to the preferred embodiments, wherein the photon source is a UV light source. The use of other photon sources will be well within the skill of those in the art in view of this disclosure.

[0021] The wavelength of the UV light exposure can be emitted as a narrow wavelength or as a broadband spectrum. Preferably, the UV light exposure is emitted as a broadband spectrum. As used herein, the term "broadband spectrum" refers to a radiation source having at least one wavelength band having a full-width half-maximum greater than about 10 nanometers (nm), with preferably greater than about 100 nm more preferred, and with greater than 200 nm even more preferred. The term full-width half-maximum (FWHM) is hereinafter defined as the width across a wavelength profile when it drops to half of its peak, or maximum value.

[0022] Preferably, the UV radiation comprises wavelengths of about 150 nanometers (nm) to about 500 nm, with about 200 nm to about 400 nm more preferred. The energy incident to the low k dielectric surface is preferably, on average, about 10 milliwatts per square centimeter (mW/cm^2) to about 1 watt (W/cm^2). The exposure times are directly dependent on the intensity of the light source (as well as other factors). In terms of throughput, the exposure times are preferably less than about 180 seconds, with less than about 60 seconds more preferred, and with less than about 30 seconds even more preferred.

[0023] Simultaneously with, or subsequent to the UV light exposure, it is preferred that

the substrate is subjected to plasma, or heat or vacuum or a combination comprising two or more of the foregoing processes. The plasma is preferably an oxygen free plasma such as is described in U.S. Patent No. 6,281,135 to Han et al., herein incorporated by reference in its entirety. Preferably, the oxygen free plasma is generated from a gas composition comprising an inert gas and optionally, a hydrogen bearing gas.

[0024] The hydrogen bearing compounds include those compounds that contain hydrogen, such as for example, hydrocarbons, hydrofluorocarbons, hydrogen precursor gas, hydrogen gas, and hydrogen gas mixtures. Preferably, the hydrogen bearing compound is a non- flammable hydrogen gas mixture containing an inert gas such as nitrogen.

[0025] Preferred hydrogen precursor gases are those that exist in a gaseous state and release hydrogen to form reactive hydrogen species such as free radical or hydrogen ions under plasma forming conditions. The gas may be a hydrocarbon that is unsubstituted or may be partially substituted with a halogen such as bromine, chlorine or fluorine, or with oxygen, nitrogen, hydroxyl and amine groups. Preferably, the hydrocarbon has at least one hydrogen and from one to twelve carbon atoms, and more preferably has from three to ten carbon atoms. Examples of suitable hydrogen bearing gases include methane, ethane, ammonia, and propane.

[0026] Preferred hydrogen gas mixtures are those gases that contain hydrogen gas and an inert gas. Examples of the inert gas include argon, nitrogen, neon, helium or the like. Especially preferred hydrogen gas mixtures are so-called forming gases that consist essentially of hydrogen gas and nitrogen gas or hydrogen gas and helium, or hydrogen gas and argon. Particularly preferable is a forming gas, wherein the hydrogen gas ranges in an amount from about 3 to about 5 percent by volume of the total forming gas composition due to safety considerations.

[0027] Plasma asher devices particularly suitable for use in the present disclosure are downstream plasma ashers, such as for example, those microwave plasma ashers available under the trade names GEMINI ES, ES3, or ES3I, and commercially available from Axcelis Technologies. Portions of the microwave plasma asher are described in U.S. Pat. Nos. 5,498,308 and 4,341,592, and PCT International Application No.

WO/97/37055, herein incorporated by reference in their entireties. The disclosure is not limited to any particular plasma asher in this or in the following embodiments. For instance, an inductively coupled plasma reactor can be used.

[0028] The amount of heat applied to the substrate will depend on the thermal stability of the particular low k dielectric layer as well as the other layers and components already formed in the substrate. The substrate is preferably exposed to heat of sufficient intensity and duration to cause the contaminants to diffuse out of the low-k dielectric layer and volatilize without causing degradation of any other components or layers in the substrate. Preferably, for porous or non-porous doped oxide low k materials the wafer is heated from about 20 ° C to about 400 ° C, with about 100 ° C to about 300 ° C more preferred. Preferably, for organic low k materials the wafer is heated from about 80 ° C to a maximum of about 180 ° C. The maximum temperatures for organic dielectrics are dependent on the intrinsic properties of the organic low k material used and can be determined by thermal analysis techniques known to those skilled in the art. The temperature may be step-wise increased during processing or remain static throughout the drying process.

[0029] A vacuum, if employed, is preferably operated at about 1 mTorr to about 100 mTorr, with about 1 mTorr to about 50 mTorr more preferred, and with about 1 mTorr to about 10mTorr even more preferred.

[0030] Figure 1 illustrates an exemplary exposure tool 10 suitable for practicing the drying process. The exposure tool 10 generally includes a process chamber 12 and a radiation source chamber 14. The process chamber 12 includes a chuck 16 on which a substrate 18 is disposed. Optionally, the chuck 16 or process chamber 12 may be adapted to provide a heat source (not shown) for heating the wafer during processing. An example of optional heating is a heated chuck. The exposure tool 10 further includes a radiation source 20 and a plate 22 may be disposed between the radiation source 18 and the chuck 16. Conduits 24 are disposed in fluid communication with the process chamber 12 for purging the chamber 12, regulating a pressure within the process chamber 12, and the like. The exposure tool 10 may further include additional features such as the structural features described in U.S. Patent No. 4,885,047 to Matthews et al., incorporated herein by reference in its entirety, for

providing a uniform exposure of light to the wafer surface.

- [0031] The drying process includes loading the substrate 18 into the process chamber 12 and exposing the substrate 18 to UV radiation emitted by the radiation source 20. Preferably, the process chamber 112 is configured for automatic handling such that manual handling of the substrate 18 is eliminated. In a preferred embodiment, the process includes purging the process chamber 12 with one or more inert gases to remove the air within the process chamber 12 and then exposing the substrate 18 to UV radiation. Suitable inert gases for purging air from the process chamber 12 include, but are not limited to, nitrogen, argon, helium, forming gas, combinations comprising at least one of the foregoing gases, and the like. Simultaneous with or subsequent to the UV radiation exposure, the substrate may be subjected to heat and/or a vacuum for removing the volatile components from the low k dielectric layer.

Examples

- [0032] In this example, a porous doped oxide low k dielectric layer with a thickness of approximately 1 micrometer was spin coated onto a silicon substrate, cured, and exposed to ambient moisture. The peaks associated with moisture and contaminant absorption can be readily observed in an FTIR spectra of the substrate at wavelengths of about 3000 to about 3400 angstroms and at about 1400 angstroms.
- [0033] The substrate was then placed in a UV process chamber having features similar to that shown in Figure 1 and purged with nitrogen. The substrate was then exposed to a UV radiation having a broadband wavelength spectrum ranging from 220 to 400 nm. The exposure time was 30 seconds and the wafer was heated to 240 °C during the exposure.
- [0034] Referring now to Figure 1, an FTIR was obtained of the substrate before and after the UV drying process. The results clearly show that moisture is removed from the low k dielectric surface as demonstrated by the absence of peaks at about 3000 to about 3400 and about 1400 cm^{-1} .
- [0035] Advantageously, the process can be used to remove contaminants from a low k dielectric layer, thus avoiding degradation that can occur because of the adhered, adsorbed, and/or trapped contaminants. The photon mediated drying process is

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